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The principal objective of this research was to develop a water resistant protective coating in order to render water soluble glass suitable for utilization as a container structure. Two alternative approaches can be used to apply such coatings: 1) apply an inorganic coating (this is currently being done in another research group using vapor deposition methods), or 2) apply an organic or polymer coating. The research described here deals with the development of the latter approach. The final coated structure might be employed as a container for such items as soft drinks, beer, food, detergents, etc.

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FORWARD

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Progress Report No. 1 "Protective Oxide Coatings for Glasses by Chemical Vapor Deposition"

Progress Report No. 2 "Mechanical Properties of Water Soluble Silicate Glasses"

Progress Report No. 3 "The Rate of Dissolution of Sodium Silicate Glasses in Aqueous Solutions"

A fifth progress report will be submitted to the Environmental Protection Agency in August 1971 and a sixth in December 1971.

TABLE OF CONTENTS

Chapter		Page
I.	INTRODUCTION AND LITERATURE SURVEY	1
II.	EXPERIMENTAL PROCEDURE	19
	Glass Sample Preparation	19
	Coating Application	20
	Coating Evaluation	23
III.	RESULTS AND DISCUSSION	30
	Surface Pretreatments	30
	Outer Barrier Coatings	37
	Characterization of Successful Coating	41
IV.	CONCLUSIONS	55
V.	RECOMMENDATIONS	59
LITERATURE CITED		61
APPENDIX		65
ABSTRACT		75

LIST OF FIGURES

Figure		Page
1.	Two Dimensional Representation of Sodium Silicate Glass Structure Near the Glass Surface	8
2.	Relationship Between Bond Strength to Glass and Polarity of Common Polymeric Materials	10
3.	Commercial Adhesives Most Desirable for Glass . . .	14
4.	Coated Glass Rod Sample Prepared for Testing. . . .	22
5.	Coated Glass Rods Undergoing Exposure to Hot Water with Continuous Agitation.	25
6.	PVHP-Elvacite 6014 Coated Tumbler	28
7.	Typical Effect Due to Liquid Accumulation Under The Coating, Prompted by Osmotic Pressure Phenomena.	35
8.	Sodium Permeation Rate for Saran Coated Glass Rod Illustrating Coating Deterioration at 60°C . .	38
9.	Dissolution Rate of 65% SiO_2 - 35% Na_2O Glass Rod (approximately 3 mm diameter, at 1 inch immersion) in Distilled Water at 25°C with Continuous Agitation	43
10.	Sodium Permeation Rate for PVHP-Elvacite 6014 Coated Rod (approximately 3 mm diamter, 1 inch immersion) in Distilled Water with Continuous Agitation at Various Temperatures.	44
11.	Sodium Permeation Rate for PVHP-Elvacite 6014 Coated Rod (approximately 3 mm diameter, at 1 inch immersion) in Phosphoric Acid Solution (pH = 2.57) with Continuous Agitation at Various Temperatures	45
12.	Sodium Permeation Rate for PVHP-Elvacite 6014 Coated Rod (approximately 3 mm diameter, 1 inch immersion) in Barium Hydroxide Solution (pH = 10.7) with Continuous Agitation at Various Temperatures	46

Figure Page

13. Sodium Permeation Rate for PVHP-Saran F-310 Coated Rod (approximately 3 mm diameter, 1 inch immersion) in Distilled Water with Continuous Agitation at Various Temperatures . 47

14. Arrhenius Plot to Examine Sodium Permeation Rate as a Function of Temperature and Solution pH . 49

15. Sodium Permeation Rate at Room Temperature in Distilled Water with Continuous Agitation. . . 51

WATER-RESISTANT COATINGS FOR SURFACES OF WATER SOLUBLE GLASS

CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

Improperly discarded containers, such as glass bottles or metal cans, constitute not only unpleasing litter, but also provide homes or water receptacles for common disease carriers such as rodents or mosquitoes. Furthermore, broken bottles and sharp-edged metal containers are a major hazard in streets, playgrounds and parks. Unlike most metal containers which will eventually corrode and disintegrate, glass will last indefinitely. With the rising costs of pick-up and disposal of litter and trash, and problems of diminishing landfill sites, it has become increasingly difficult to deal with the disposal of glass containers.

Since littering cannot be stopped completely, it has been suggested to develop packaging materials of biodegradable compositions. However, suitable container materials have not yet been developed or fully accepted. Alternatively, water soluble materials could be used in the future provided that satisfactory fabrication methods can be established. For the purposes of this research, water soluble glass has been considered as such a container material because glass is inexpensive, strong and presently accepted for container usage.

Sodium silicate glass is water soluble. Present glass containers are generally manufactured from a related

silicate system, modified with the alkaline earth oxides, alumina, and/or boric oxide (1). These latter additions render the glass virtually insoluble in water (2). Soda-lime glass, the common container glass, has a typical composition in the following ranges: CaO 6-12%, SiO_2 58-74% and Na_2O 13-19% (1). A sodium silicate glass composition of 65% SiO_2 and 35% Na_2O has been chosen for this research in order to obtain desirable solubility and working characteristics. Sodium silicate glasses with a smaller percentage of silicon dioxide have a higher dissolution rate in water, but are more expensive, more viscous when molten and render the fabrication of containers more difficult (3). Furthermore, dissolved glass of such a base-rich composition would be difficult to neutralize. A higher percentage of silica would also be detrimental since reduced dissolution rates would then be experienced (3). Soluble silicates are presently used in industry as adhesives, cleaners, cements, deflocculents and protective coatings (4). The sodium silicate glass can be dissolved in water to produce sodium hydroxide (NaOH) and silica gel ($SiO(OH)_2$). Sodium hydroxide is a base that would probably be neutralized in soil by widely occurring acidic constituents. Silica gel would occur as a white gel-like substance that does not pose any obvious toxic threat to the environment. It is commonly used as a particularly non-corrosive desiccant. Actual detailed studies of the dissolution products

of sodium silicate glass and their effects upon the environment are planned for future investigations.

Existing glass manufacturing equipment and methods can be applied to produce containers from the 65% SiO_2-35% Na_2O glass. For demonstration purposes, sodium silicate glass containers were actually manufactured for this research project by the Anchor Hocking company (Lancaster, Ohio) in December, 1970.

Because increased percentages of sodium carbonate are required in the formulation of this particular glass composition, the cost of raw materials is enhanced to some extent. But this expense will be partially balanced by lower fuel costs, due to the fact that the glass melts at a lower temperature and requires less heat for processing.

The principal objective of this research was to develop a water resistant protective coating in order to render water soluble glass suitable for utilization as a container structure. Two alternative approaches can be used to apply such coatings: 1) apply an inorganic coating (this is currently being done in another research group using vapor deposition methods), or 2) apply an organic or polymer coating. The research described here deals with the development of the latter approach. The final coated structure might be employed as a container for such items as soft drinks, beer, food, detergents, etc.

The effectiveness of a barrier coating depends upon two inter-related phenomena: 1) adhesion and 2) corrosion resistance. In reviewing the literature on corrosion resistant polymeric coatings, many commercially available polymeric materials are cited as forming excellent corrosion resistant barriers, but in order for them to be useful in this research they must be able to adhere to glass. Authors such as Seymour and Steiner (5) exclude such coatings for glass because of the inherent corrosion resistance exhibited by most glasses.

Adhesion to glass surfaces, and more particularly, polymer adhesion to glass surfaces, is a subject of wide interest since such applications as safety glass, double glazed windows, glass-rubber assemblies, glass-metal assemblies and glass window installations depend upon the use of glass adhesives (6).

In general, adhesion phenomena can be divided into two categories: 1) specific adhesion, or 2) mechanical adhesion (7). Specific adhesion arises due to molecular forces, while mechanical adhesion is thought to occur due to the interlocking of adhesive and surface irregularities. Most authors feel that mechanical adhesion plays only a small part in the bonding of irregular surfaces (7), and cite the subsequent increased surface area upon which molecular forces act as the major cause for increased adhesion on a roughened surface (8). Specific adhesion can occur as the

result of primary or secondary molecular forces. Primary molecular forces deal with chemical reactions and molecular structural changes resulting from ionic, metallic or covalent bonds (9). Inorganic coatings, such as those involved with chemical vapor deposition processes, are probably bonded through primary forces, while organic coatings are generally bonded by the interaction of secondary molecular forces (10). Secondary molecular forces, which appear to be most important in this research, can be further divided into those dealing with dipole-dipole interactions (dipole forces), permanent and induced dipole interactions (induction forces), and instantaneous dipole interactions involving non-polar materials (dispersion forces) (9). Secondary molecular forces are small--the attractive potential energy between two molecules being proportional to the reciprocal sixth power of their separation distance (11). Dipole-dipole interactions are the strongest among the secondary forces, and attachment can be expected to be many times stronger than that provided by dispersion forces (7).

In order to determine what type of forces are necessary to bond an organic coating to glass, it should be recognized that the sodium silicate glass structure consists of a random three dimensional and covalently bonded network, which is intimately associated with positive sodium ions.

The interior of the glass is electrically neutral, but at the surface the positive and negative charges will be slightly unbalanced due to an increased concentration of non-bridging oxygen groupings and the high mobility of sodium ions associated with them (12). In efforts to decrease surface energy, the glass is known to rapidly chemisorb water molecules from its surroundings (2). This spontaneous reaction changes the nature of the surface to generate many polar hydroxide groups (see Figure 1) and is reported to leave few oxygen atoms unreacted at the surface (10). From principles of electrostatic theory one would conclude that the surface density of ionic charges is relatively low (13); and hence, one cannot rely on electrostatic attractions exclusively in order to establish strong bonding between a coating and the glass surface.

Therefore, in order to attach a coating material directly onto such a polar surface, the contacting coating layer should possess polar characteristics that will match those of the glass, and thereby establish strong bonding through the interactions of many of these relatively weak dipole-dipole forces.

The preliminary assessment of a potential glass coating material with regard to adhesion, can be accomplished by estimating its relative polarity through the knowledge of its molecular structure. Typically, polymers containing

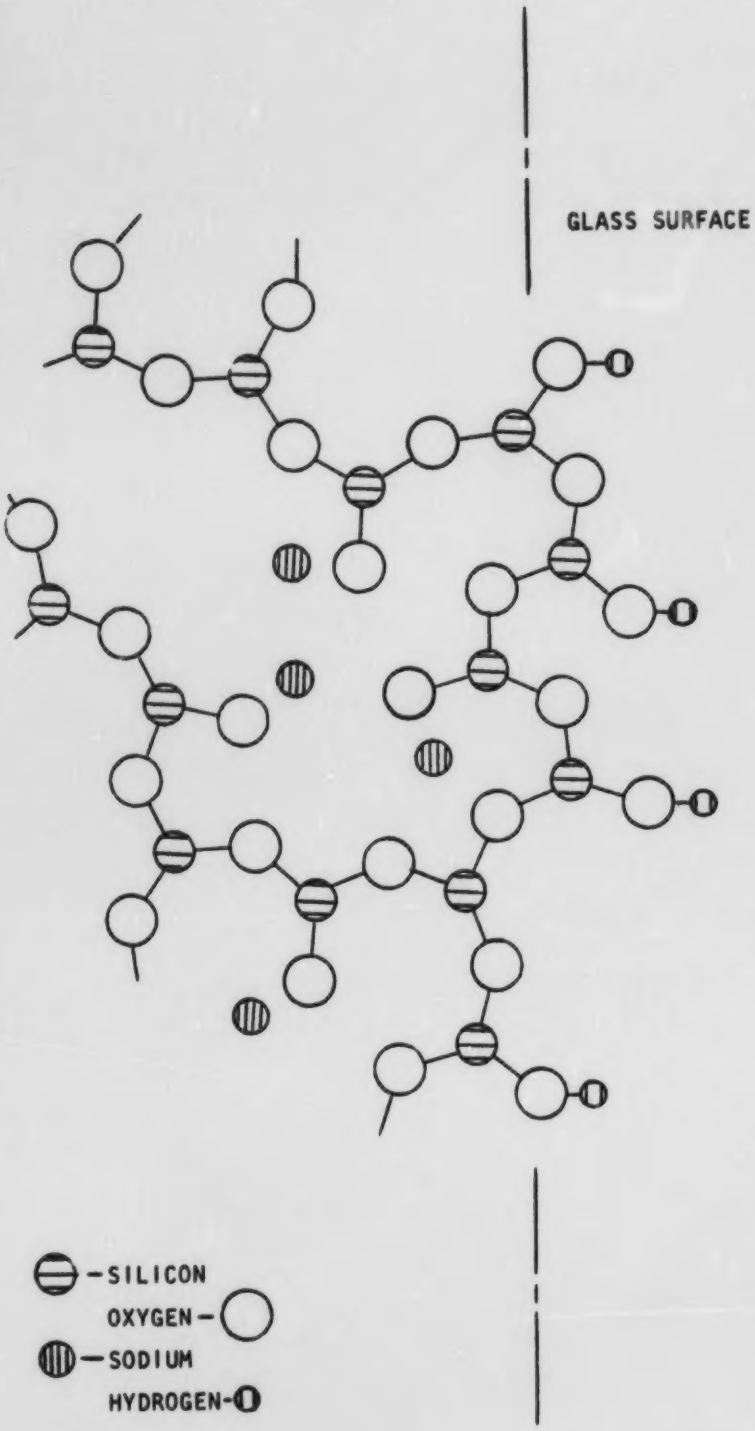


FIGURE 1. Two Dimensional Representation of Sodium Silicate Glass Structure Near the Glass Surface (after B.E. Warren (14)).

hydroxyl, carboxyl, amide, or other similar polar side groupings should participate in dipole interactions. Wetting of the surface by the coating material can also be used as a guide to the bonding potential of an untested coating; good wetting signifies strong molecular forces at the adhesional interface (7). In the interior of the coating, the molecules are surrounded in a balanced way and are subject to no net attraction in any one direction; however, at the surface, due to lack of equal surrounding charge, a net inward force exists. If work is not done at the adhesional interface to overcome this net inward attraction, the coating will form into spherical drops and will subsequently not wet the surface (15). Wetting is a necessary, though not sufficient condition for good adhesion (7). More recently, contact angle studies have been used to determine the relative polarities of adhesives and adherend surfaces in order to establish their potential suitability. Moser (16) has attempted to establish a direct relationship between polarity and mechanical bond strength for various polymers bonded to glass. (See Figure 2).

The successful glass adhesives produced during this century have been classified by Yaeger (17) into seven categories: 1) cellulose esters, 2) proteins, 3) inorganic-organic combinations, 4) acrylic and vinyl compounds, 5) rubbers, 6) acetates, and 7) miscellaneous resins. Nitrocellulose, first described by Wood in 1906 (18) and later

Polymer	Bond Strength under Tensile Load (psi)	Polarity (Contact Angle) Degree
Polyvinyl acetate ("Bakelite" AYAF)	550	25-28
Polyvinyl acetate-dibutyl phthalate	1200	18-20
Polyvinyl chloride-acetate ("Bakelite" VMCH)	400	65-67
Polyvinyl chloride-acetate ("Bakelite" VYHH)	100	60-62
Polyvinyl butyral	600	30-32
Polyvinyl chloride-acetate alcohol	1200	24-26
Polyvinyl butyral-dibutyl phthalate ("Bakelite" XYHL)	1200	18-20
Methyl methacrylate	0-100	62-64
N-propyl methacrylate	200	63-65
Polyvinyl alcohol	400	14-15
Polyvinyl chloride	0-100	66-68
Cellulose nitrate	200	36-37
Ethyl cellulose	0- 50	60-61
Phenolic ("Durez" 12987)	500	22-24
Phenolic ("Bakelite" BR 17620)	300	38-40
Substituted phenol aldehyde ("Bakelite" BV-1112)	100	43-44
Aryl sulfonamide formaldehyde ("Bakelite" MS-80)	100	33-35
Styrene butadiene ("Pliolite" S-5)	0-100	70-72
Cyclized rubber ("Pliolite" S-50)	100	37-40
Neoprene Type GN-A	0-100	35-38

FIGURE 2. Relationship Between Bond Strength to Glass and Polarity of Common Polymeric Materials (after Moser (6)).

patented by Benedictus (19) in 1914, was the first glass adhesive used for an industrial application, namely in the production of safety glass (17). Through the next twenty years nitrocellulose continued in prominence for this use, although the composition had a tendency to yellow, was temperature sensitive, and eventually would creep away from the glass surface to form voids. Authors now feel that nitrocellulose did not truly bond to the glass, but rather provided an air-free gel between the glass surfaces which caused the glass to be held in place by atmospheric pressure (20).

Gelatin, a proteinaceous material related to common animal glues, was later employed by Benedictus to bond celluloid to glass surfaces. Waine (20) states that the adhesion of gelatin to glass has probably never been improved upon by the most modern adhesives. Eley (21) suggests that gelatins and other proteins, as well as urea-formaldehyde, phenol formaldehyde, and certain rubbers which are used as glass adhesives, contain chemically reactive groups and possibly form chemical bonds with the glass surface. The major problem with gelatin is that it is water soluble and thus necessitates moisture control in the bonding area if the bond is to be maintained.

The discoloring and instability of nitrocellulose was overcome by the subsequent use of cellulose acetate. By increasing its free hydroxyl content, cellulose acetate becomes a tenacious glass adhesive, but as with gelatin, it is moisture sensitive (20).

Ethyl-orthosilicates, inorganic-organic combinations, were also prepared as glass adhesive compositions for safety glass applications although they are also moisture sensitive (20).

One of the first synthetic polymers produced, polymethyl acrylate or "plexigum" was used as a glass adhesive, but as evidenced by Moser's polarity studies (6) of non-polar methyl methacrylate, it does not bond to glass but rather provides an air tight seal allowing adhesion by "atmospheric stick" (20).

With the advent of more synthetic plastics, cellulose derived materials were slowly replaced by adhesives prepared specifically for the purposes of glass adhesion. One such adhesive is polyvinyl butyral which was originally prepared from polyvinyl alcohol that had undergone acetal condensation with butyraldehyde in the presence of acid. This process produces a clear, tough polymer that will adhere to glass if a limited quantity of butyraldehyde is used so that some free hydroxyl groups will remain and establish polar interactions with the glass surface.

Polyvinyl butyral, while not being water soluble, is subject to attack by moisture, and if satisfactory bonding is to occur the moisture content must be kept below 0.5% (20). Since 1936 polyvinyl acetal and polyvinyl butyral resins have been used as glass adhesives in the production of safety glass (17).

During the 1940's bifunctional organo-silanes were developed as fiber finishes and were later used to promote polymer adhesion to glass surfaces (17). At present, various formulations of organo-silanes are commercially available. Union Carbide produces over two dozen different silanes for specific adhesion applications (22).

In reviewing presently available commercial glass adhesives, two basic types are commonly employed: 1) polymers which require heat setting or the addition of hardeners or 2) polymers supplied dissolved in solvents which dry by evaporation of the solvent. Heat curing adhesives, because of their curing requirements and occasional high shrinkage rate, often induce stresses in the glass surface. As cited by Moser (6) care must be taken not to inflict high stress concentrations as they have been known to cause failure of the glass well below its normal tensile strength. A chart of commercially available adhesives, recommended by Moser to be most desirable for glass adhesion, is given in Figure 3. Structural adhesives, such as phenolic polyvinyl butyral and modified phenolics, are cited by Moser as having

Trade Name	Chemical Type	Strength (psi)	Weathering Quality
"Butacite," "Butvar"	Polyvinyl Butyral	2000 - 4000	Fair
"Bostik" 7026, FM-45, FM-46	Phenolic Butyral	2000 - 5500	Excellent
N-199, "Scotch-weld"	Phenolic Nitrile	1000 - 1200	Excellent
"Pliobond" M-20, EC847	Vinyl Nitrile	1200 - 3000	Fair to Good
EC711, EC882 EC870	Neoprene	800 - 1200	Fair
EC801, EC612	Polysulfide	200 - 400	Excellent
EC526, R660T, EC669	Rubber Base	200 - 800	Fair to Poor
"Silastic"	Silicone	200 - 300	Excellent
"Rez-N-Glue," duPont 5459	Cellulose vinyl	1000 - 1200	Fair
"Vinylite" AYAF, 28-18	Vinyl acetate	1500 - 2000	Fair
"Araldite," "Epon" L-1372, ERL-2774, R-313, C-14, SH-1, J-1152	Epoxy	600 - 2000	Fair to Good

FIGURE 3. Commercial Adhesives Most Desirable for Glass (after Moser (6)).

excellent weatherability characteristics, but are of the heat curing variety. Guttman (23) cites cyanoacrylates as being strong glass adhesives, but are not suitable for prolonged exposure to water. Delmonte cites (15) the use of n-butyl methacrylate as an optical adhesive which exhibits little temperature sensitivity. Polyvinyl butyral is cited by Moser (6) for producing excellent adhesion, but the weatherability is only fair. Phenolic-nitrile rubber formulations require curing to produce their excellent bonding and moisture resistance, but a film of this material becomes brittle after curing and chipping of the glass can take place (6). Other adhesives having excellent weatherability include the polysulfides and silicones; however, both exhibit low strength. Commercially available lacquers or coatings are too numerous to mention; companies such as Dow Chemical, Du Pont, Union Carbide, Monsanto, Thiokol, etc., all make lacquers suitable for a variety of coating substrates other than glass, for corrosion resistant uses. However, the only real commercial glass binders besides the adhesives are the adhesion promoters or finishes such as the organo-silanes.

Because of the tedious precautions involved and the technical difficulties present with heat curing adhesives, polymers dissolved in solvents were thought to be a better

choice for water soluble glass coatings that would eventually have to be applied industrially in large quantities.

Under dry conditions and at room temperature, many commercial glass adhesives are cited as exhibiting excellent adhesion. However, if the adhesive bond is subject to high humidity or is placed in water, failure routinely occurs (24). One of the more severe requirements for the water soluble coating is then seen to be that of continuing good adhesion under such adverse conditions. Obviously, for water soluble glass to be usable for such end uses as containers for food, soft drinks, beer, detergent, etc., the coating must resist attack by aqueous solutions. Furthermore, it must withstand the attack of high temperature aqueous solutions, since pasteurization in some industries (beer for example) is performed in the finished container and commonly carried out at temperatures of about 150°F (25). The principal weakness of most commercial glass adhesives is predicated by their polar nature; in being polar the material often becomes susceptible to attack by the polar molecules of water. For example, polyvinyl alcohol has been found to bond to glass extremely well (6), but the polymer is dissolved or swollen (depending upon its molecular weight) by water. The satisfactory coating must be, to an extent, bifunctional; it must contain polar groups for bonding to glass, yet it must withstand attack by polar water molecules.

Another possible mode of approaching this polymer bifunctionality problem also exists; by changing the glass surface according to etching methods or chemical vapor deposition techniques, one might be able to attach suitably a relatively non-polar commercially available water resistant polymer coating material as an outer barrier coating. Surface etching techniques could be carried out in aqueous solutions and might proceed by the leaching of monovalent sodium ions and by replacing them with divalent ions of similar size, which could then react further with subsequently supplied ions to form insoluble, non-polar precipitates on the glass surface. Alternatively, chemical vapor deposition techniques might also be used to change the glass surface. Numerous commercially available non-polar lacquers or formulations such as Saran, could then be applied and tested as outer coating barriers.

Another approach to the problem would incorporate two coatings; the first, such as a bifunctional organo-silane, could be applied to alter the glass surface to provide a relatively non-polar surface for seating a water resistant non-polar lacquer; the second coating could then be applied to provide a water resistant barrier.

In summary, a coating is needed that will meet the following requirements:

1) It must wet the glass (or altered glass) surface, and in the case of bonding directly to the glass, provide sufficient numbers of polar groups so that good adhesion can be established.

2) It should allow little solution permeation.

3) It should have a generally acceptable appearance.

4) It must maintain the above requirements in high temperature aqueous solutions.

5) It should be suitable for the large scale production of soluble glass containers.

6) It should allow an economically feasible container to be manufactured.

The objective of this research was to determine a coating for water soluble, sodium silicate glass that would satisfy the previously stated requirements.

CHAPTER II

EXPERIMENTAL PROCEDURE

A. Glass Sample Preparation

Rods of sodium silicate glass were used as test samples in this research so that dip-coating techniques could be easily carried out, and drying of the partially coated rods could be accomplished without contamination. Furthermore, it was thought that by using drawn rods and not molded shapes, the surface of the glass samples would be less contaminated and more consistent in composition.

The glass rods utilized in this research were made from a melt of 65% SiO_2 - 35% Na_2O sodium silicate glass. The raw materials used to produce this glass, i.e., silicon dioxide and sodium carbonate, were of reagent grade supplied by the Pennsylvania Glass-Sand Co. and J. T. Baker Chemical Co., respectively. After careful weighing, the SiO_2 and Na_2CO_3 were either mixed in a polyethylene bag with vigorous agitation for 15 minutes, or were mixed in a vee-blender for approximately 30 minutes. The blended mixture was emptied into high temperature crucibles and fired in a "Hevi-Duty" glowbar furnace at approximately 2300°F. After soaking for at least one hour, the furnace temperature was lowered to approximately 1600°F, and each crucible was removed and placed on firebricks and held in place using tongs. A heated cast iron "bait" of approximately 1.5 cm in diameter

was then lowered using an attached steel bar into the glass melt. As the color of the melt changed from red to yellow the "bait" was withdrawn from the glass and gradually hand raised at a speed that yielded a uniform rod of approximately 3 mm diameter. A rod of approximately 1.3 meters in length was routinely drawn and broken off at the top of the crucible. The crucible was returned to the furnace and was allowed approximately five to ten minutes to again reach drawing temperature. The glass rod was broken near the end of the "bait" and was cut into two sections. The rods were placed in an annealing furnace at 800°F. When the drawing was concluded the annealing furnace was shut down and allowed to cool over night. The "bait" was cleaned by tapping the glass covered end and shattering the adherent glass. It was then re-heated prior to the next drawing procedure.

After annealing, the rods were cut to 6 cm lengths with a glass file, both ends of the rods were fire polished and the prepared glass rods were stored in a desiccator for future use.

B. Coating Application

The initial approach taken in this research was that of altering the glass surface by etching techniques. The fire polished sodium silicate glass rods were soaked for specific lengths of time in various metal salts and

hydroxides of various concentrations. (See Appendix I for specific etching treatments.) Upon removal, they were washed in sodium sulfide or sulfite, or potassium hydroxide solutions. They were further washed in distilled water and allowed to dry in a desiccator. The etched rods were dip-coated with various commercial lacquers; these polymeric solutions were either prepared according to company literature or were supplied in solution form. The dip-coating procedure included immersing 5 centimeters of the rod in the polymer solution for about 5 seconds and upon removal, the rod was suspended in a vertical position to facilitate the elimination of excess coating accumulations. The last drop of coating solution was removed from the rod by touching the latter to the surface of the coating solution. The coatings were generally allowed to dry in a desiccator at room temperature; however, Saran coatings were found to be more effectively dried at 200°C for 45 seconds. The coating and drying procedure yielded a coating of fairly uniform thickness. The coating thicknesses were calculated by measuring the change in diameter of uncoated and coated rods using both calipers and a feeler gage.

In order to protect the upper edge of the coating, the uncoated portion of the rod was covered with tightly fitting rubber tubing. A rod prepared for testing can be seen in Figure 4.

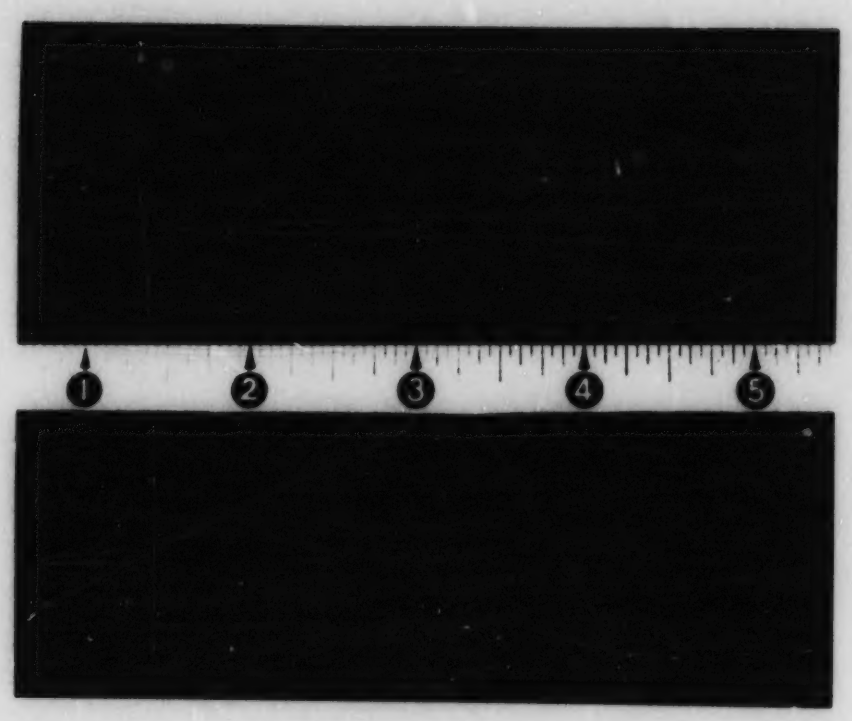


FIGURE 4. Coated Glass Rod Sample Prepared for Testing.

Bifunctional organo-silanes and silicones were applied to sample glass rods by either the previously described dipping techniques or by vapor application methods described in the company literature (26). All lacquers used in subsequent tests were applied by the dipping procedure previously described. All rods were equipped with tightly fitting rubber tubing (as seen in Figure 4) prior to immersion in aqueous test solutions.

C. Coating Evaluation

The water absorption characteristics of the coatings were measured by weighing the coated glass rods before and after exposure at an immersion depth of one inch in water; the solution was maintained at 25°C for 72 hours. The observed difference in weight permits the calculation of the percent water absorption. Other water absorption tests were performed using a thermogravimetric analyser equipped with a two-pen, strip chart recorder to simultaneously measure weight loss and specimen temperature versus time.

In order to determine the effectiveness of coatings in preventing the dissolution of glass, coated glass rods were suspended in 250 ml Erlenmeyer flasks containing 100ml of distilled water, such that one inch of the coated end was immersed. The unagitated water was maintained at a constant temperature (60°C ±1°C) using a temperature controlled bath. At a given interval of time (generally 120

minutes) samples were removed by pipette and transferred to aged glass sample bottles. The samples were tested for sodium ion concentration on an Evans Electroselenium Ltd. (EEL) atomic absorption spectrophotometer. The coatings were also examined for deterioration and weakening of their adhesive bond to the glass surface. For purposes of such evaluation a circumferential cut in the coating was made approximately 1.25 cm from the bottom of the coated end. The severed section of coating was grasped and held immobile using finger pressure while the uncoated end of the rod was pulled away from this immobile coated end. A coating formulation that passed these tests was used again to coat other soluble glass rods which were then tested using the same procedures at higher water temperature (usually 70°C). If good results were again exhibited, more similarly coated rods were extensively tested for sodium ion concentration at temperatures ranging from 45 - 75°C. The glass rods were routinely suspended in Erlenmeyer flasks containing 200 ml aqueous solutions allowing one inch of the coated end to be immersed (see Figure 5). Different sets of samples were tested in distilled water, in basic solution (in barium hydroxide at pH=10.7) and in acid solution (in phosphoric acid at pH=2.57). Barium hydroxide was chosen to make the basic solution because it did not interfere with the determination of sodium ion concentration as made on the Perkin-Elmer atomic absorption spectrophotometer;

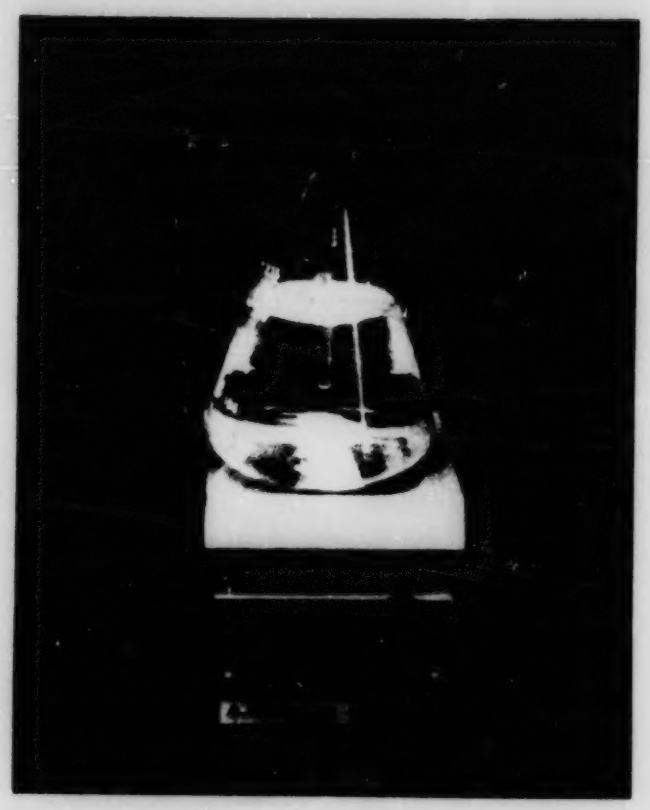


FIGURE 5. Coated Glass Rod Undergoing Exposure to Hot Water with Continuous Agitation.

with other common basic solutions using alkali metal family (Li, K, Rb, Cs, Fr) compounds, inaccuracy in the determination of sodium ion concentration would result due to the similiarities in spectral response; and the spectrophotometer would then be incapable to measure the sodium concentration accurately (27). Furthermore, barium hydroxide allows aqueous solutions to be easily prepared and to attain relatively high values of pH. Phosphoric acid was used in making the acidic solution because it is commonly found in soft drinks, and it permits the attainment of pH values in the range encountered in soft drinks. During testing, the solutions were maintained at constant temperature ($\pm 0.5^{\circ}C$) and kept under continuous agitation using a Teflon-coated magnetic stirrer. At standard intervals, i.e., 20, 40, 60, 90, and 120 minutes of elapsed exposure time, 10 ml samples were transferred by pipette into polyethylene sample bottles. The samples were tested for sodium ion concentration in parts per million using the Perkin-Elmer Model 402 atomic absorption spectrophotometer. The sodium concentrations (in ppm) were plotted versus immersion time. Many of the tests involved repeated use of the same sample rods so that coating thickness, glass surface area and immersed surface area were effectively held constant.

In order to determine the relative amounts of copolymer components of one specific coating (Dow Chemical's Saran), an analysis for the amounts of carbon, hydrogen and nitrogen

present was run on an F & M Carbon-Hydrogen-Nitrogen Analyzer, Model 185. Knowing the percentage of these elements permits the calculation of the specific weight and mol percent of each copolymer component.

Other barrier coating formulations that were not revealed in detail through company literature (DuPont's Elvacites) were characterized by infrared analysis. Thin films of the polymer formulations were formed on a polyethylene sheet; they were then mounted, analyzed and compared to known compositions for each identification of characteristic differences in bonds and chemical groupings.

An examination of the solvent release characteristics of the Elvacite 6014 coating material was made using a Fisher thermogravimetric analyser (equipped with a Cahn Electrobalance). These studies enabled a determination of the diffusion coefficient for the solvent within the polymer material. A thin (2 mil) coating of Elvacite 6014 was applied to a prepared surface area on a thin titanium plate. The plate, with the wet coating, was suspended in a heating tube maintained at a constant temperature. A mild vacuum, approximately 300 mm Hg, was applied while the weight loss of the sample was measured versus time, using a strip chart recorder.

For demonstration purposes, glass tumblers (See Figure 6) were manufactured by the Anchor Hocking Glass Company

FIGURE 6. PVHP-Elvacite 6014 Coated Tumbler.

(Lancaster, Ohio). The tumblers of soluble glass were coated by dipping into large containers of solution. They were removed with tongs from the dipping containers and placed on three-point ceramic stilts for drying in a hood. Common soda lime glass beer bottles were also coated with our coating formulation so that lubricity tests of the coating could be conducted. The coatings were tested under wet and dry conditions on an apparatus built for the Anchor Hocking research facilities and designed from an apparatus described in Technical Engineering-Methods Research Testing, by Daniel M. Mahoney of Owens, Illinois.

CHAPTER III

RESULTS AND DISCUSSION

A. Surface Pretreatments

1. Etching Treatments. The most severe requirements of a coating for water soluble glass are resisting deterioration and maintaining strong adhesion under attack by hot water. Over one hundred types and combinations of polymers and etching treatments were tested (see Appendix I) before a coating was found that met all the necessary requirements set forth in the Introduction.

Using etching treatments and commercially available coating materials, several combinations were found that provided a fairly good barrier coating while maintaining strong adhesion in hot water (See Appendix I).

One of the successful etching treatments consisted of immersing soluble glass rods in a 0.5 N silver nitrate aqueous solution for 30 minutes. The treated rods were then washed in a concentrated solution of sodium sulfide. It is theorized that the silver nitrate aqueous solution dissolves the glass surface to a limited extent and leaches monovalent sodium ions; silver ions in the solution are then able to migrate into some of the vacated sites, or they become bound to the glass surface to balance the resultant negative charge excess created by the movement of the positive sodium ions. The silver ions, when washed with a

solution containing sulfide ions, could further react to form water insoluble silver sulfide on the glass surface.

Similar etching procedures by this exchange mechanism, were also found acceptable with zinc, copper and tin ions used as divalent substitutes for the leached monovalent sodium ions; water insoluble compounds generated from supplied sulfides and hydroxides were then thought to be formed on the glass surface again. Other divalent ions, magnesium and nickel, were found to be less suitable for treating the glass surface.

All of the mentioned divalent ions, when in their unsolvated states, have a smaller ionic radius than that of monovalent sodium; the ionic radius of Na^{+} = 0.97 A^{0}, while Sn^{+2} = 0.93 A^{0}, Zn^{+2} = 0.74, Cu^{+2} = 0.72 A^{0}, Ni^{+2} = 0.69 A^{0} and Mg^{+2} = 0.66 A^{0} (28). However, only those which most closely matched the ionic radius of sodium, were seen to be effective in providing a surface for strong polymer bonding. From the results it can be postulated that if substitution for sodium ions is to be made using divalent ions, the divalent ions should have ionic radii similar to that of sodium. However, tests were not run using divalent ions with radii larger than sodium, and no conclusive statements can be offered.

Although satisfactory coatings could be obtained in the laboratory using etching treatments, industrial fabrication of containers using such a process would be difficult. The

process is slow and optimization is tedious. Furthermore, contamination of the glass surface must be avoided or controlled so that uniformity of the surface composition can be maintained. This requirement is necessary since the process is dependent upon minor dissolution of the glass surface; slight changes in the surface composition will result in inconsistent surface etching. Etching solution temperature optimization was found to be difficult, since reproducible results could not be routinely obtained. Furthermore, variations in the resulting etched surfaces were occasionally observed after room temperature etching on the same glass rod. These differences are apparently due to inconsistencies in the glass surface and differences in dissolution rates. Because of the impracticality of etching techniques in an industrial process, organo-silanes and silicones were evaluated as surface pretreatments and coatings.

2. Organo-silanes and Silicones as Surface Pretreatments. Organo-silanes from General Electric were evaluated as coatings. They bonded well to the glass surface, but in hot water became brittle and peeled away from the glass surface. If used as surface primers under other barrier coatings they failed the slippage test. Union Carbide A151, vinyltriethoxy silane, A150, vinyltrichloro silane and A172, vinyl-tris-(beta-methoxy-ethoxy) silane were also evaluated as pretreatments because of their reported usage

as coupling agents between glass fibers and organic resins (22). The silanes were not effective as coatings, however, A172 exhibited considerable proficiency as a surface primer. In hot water though it allowed the slippage of the outer coating from the glass rod under moderate finger pressure.

3. Other Glass Bonding Polymeric Materials as Sub-Coatings. A chrome stearate, which has also been reported in use for promoting glass adhesion of organic resins (21), obtained from the Valchem company, bonded to the glass extremely well, but our available outer coating materials would not continue good adhesion to it in hot water.

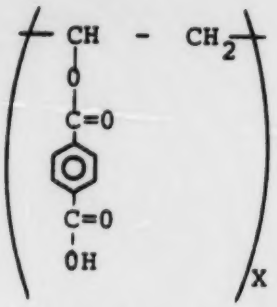
Aside from the etching techniques, suitable glass adhesion had yet to be maintained in hot water tests. Polyvinyl alcohol, a tenacious glass adhesive due to its many polar hydroxyl groups, was used as a surface pre-coating. High temperature, slow dissolving Elvanol 52-22 and 71-30 obtained from Du Pont, were used. Although polyvinyl alcohol is water soluble, it was hoped that the permeation rate of water through the outer coating would be small, and a reasonable shelf life for a coated container might be obtainable. The polymer structure provided a good surface for seating the outer coating; however, after testing in hot water the coating could be slipped from the glass rod. If the rod was left in room temperature water for extended periods of time, separation of the coating from the glass rod was also visible. As can be seen in

Figure 7, the coating has separated from the glass rod and at the bottom of the rod considerable ballooning of the coating has occurred. When water molecules permeate the coating and reach the glass surface, dissolution of some glass occurs, creating a concentrated solution under the coating. In trying to reach equilibrium, more water molecules will migrate through the coating membrane in efforts to dilute the concentrated solution underneath, in order to establish a uniform concentration on both sides of the coating membrane. This influx of water molecules generates a pressure between the surface and coating, and explains the observed tendency of some coatings to balloon away from the glass surface.

In efforts to eliminate slippage, polyvinyl butyral-dibutyl phthalate (Bakelite XYHL) dissolved in methyl ethyl ketone was evaluated as a surface precoating. Although Waine (20) states that the moisture content for polyvinyl butyral must be held below 0.5% for the polymer to show good adhesion to glass, it was hoped that polyvinyl butyral with mixed-in amounts of dibutyl phthalate added might exhibit greater moisture resistance. Bakelite XYHL exhibits low polarity and excellent bond strength (6), but when used as a precoating it also allows slippage of the coating around the glass surface after exposure to hot water.

FIGURE 7. Typical Effect Due to Liquid Accumulation Under the Coating, Prompted by Osmotic Pressure Phenomena.

In reviewing polymers containing polar side groupings for possible adherence to glass, polyvinyl hydrogen phthalate was recognized as being a possible glass adhesive. Polyvinyl hydrogen phthalate (PVHP),



provides polar carboxyl groups for dipole-dipole interaction with glass, yet its bulky hydrocarbon chain and benzene ring structures prevent its dissolution in water. The polymer was found to be soluble in methyl ethyl ketone; a solution of the polymer dries to yield a hard, transparent film. It was found that a concentration of 80 grams PVHP per liter of MEK yields a dip-coated film of approximately one mil thickness when dry. A more concentrated solution of PVHP results in a thicker film, which caused hair line cracks to occur when used in combination with the outer coating. The cracking is thought to occur due to the fact that a thick prime coating is difficult to keep from being swollen by solvents, even though a hardened barrier coating is in contact with it. As prolonged storage of the composite structure brings about a loss of vapors from the swollen layer, the top coating may become subject to stresses that

can bring about hair line cracks. If the PVHP coating is reduced to one mil thickness, cracking of the coating is not observed. If a much thinner coating of PVHP is applied, the coating blushes, perhaps due to atmospheric moisture.

B. Barrier Coatings

As outer barrier coatings, the initial tests used Saran F-310, manufactured by Dow Chemical, dissolved in methyl ethyl ketone. The polymer composition was calculated from a carbon, hydrogen, nitrogen analysis to be 82.5% by weight vinylidene chloride and 17.5% by weight acrylonitrile; this corresponds to approximately 0.72 mols of vinylidene chloride and 0.28 mols of acrylonitrile. A coating of approximately 2 mil thickness was obtained using a solution of 20% by weight Saran and the previously described dipping and drying procedure. Saran was seen to be a suitable coating material at temperatures below 60°C, but above this temperature the coating had a tendency to deteriorate. Figure 8 illustrates this point. Curve 1 is linear, from which it is inferred that deterioration of the coating is not occurring, and that the rate of membrane permeation, as measured by the concentrations of sodium ions, is the same at all times. The second curve shows a plot of sodium ion concentration versus time at 60°C, in which it is inferred that the glass dissolution rate is increasing with time to yield a non-linear trend; this is thought to be the result

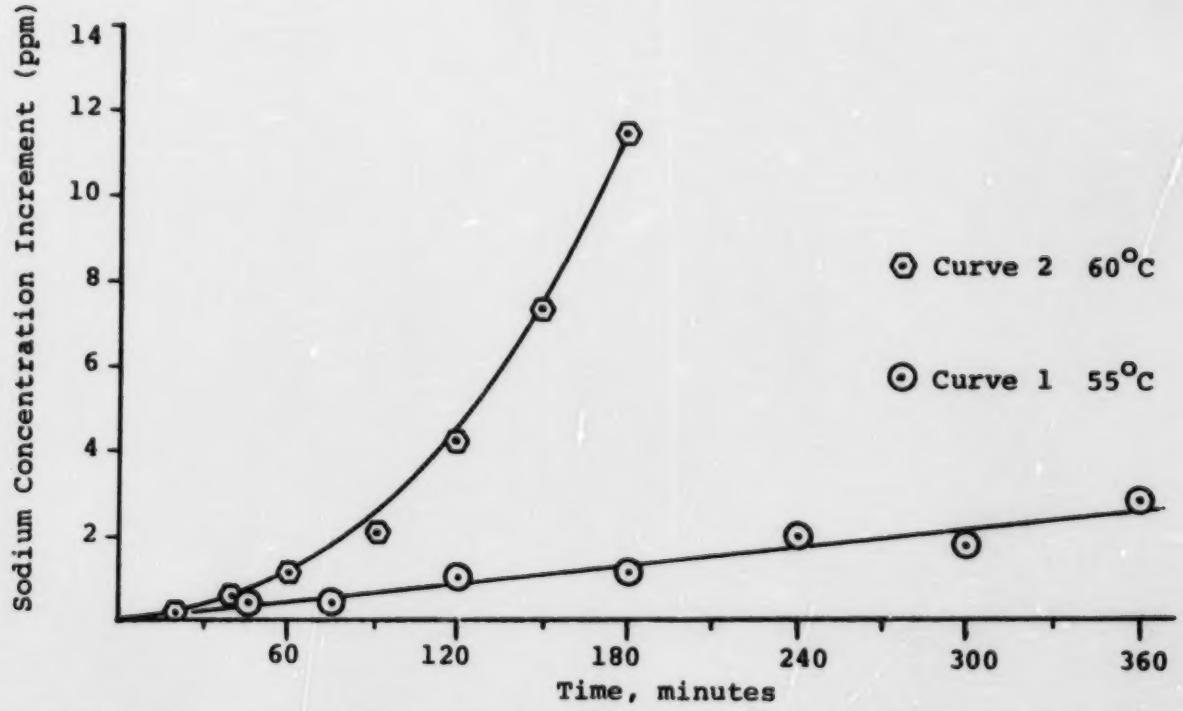


FIGURE 8. Sodium Permeation for Saran Coated Glass Rod Illustrating Coating Deterioration at 60°C.

of the deterioration of the coating. Because of Saran's reputed excellent moisture resistance, it was thought that perhaps some solvent still remained in the polymer network. Several low temperature (40°C) drying procedures were attempted, but none proved successful in improving the properties of the Saran coating. It was later revealed through private communication that in order for all of the solvent to be released from the Saran network, the coating had to be dried at 200°C for approximately 45 seconds. This drying procedure produced a coating that was clearer, tougher, and more resistant to hot water than the previously room temperature dried coatings. However, at temperatures slightly above 70°C the coating still had a tendency to deteriorate.

Using zinc sulfate and zinc chloride etching solutions, and using sodium sulfide and potassium hydroxide washes, a whole series of sample outer coatings were prepared for evaluation. (See Appendix I) Most coating formulations either became brittle and peeled away from the glass surface or allowed too much glass dissolution to occur.

Du Pont's Elvacite 6014 was found to form a tough, transparent polymeric barrier coating which allowed little dissolution of the glass even at the highest test temperatures investigated. Infrared analysis has revealed that Elvacite 6014 is a methyl methacrylate copolymer with some butyl methacrylate groupings. In addition, the Elvacite

6014 polymer also contains some carboxyl groups for increased adhesion onto polar surfaces (29). The Elvacite polymer was obtained in solution form for direct application onto pretreated glass rods. This solution containing 40% solids was supplied dissolved in 80% toluene and 20% isopropanol. Because of the additional polar groupings, several virgin glass rods were coated with Elvacite 6014 and preliminarily tested; however, bubbling of the coating and subsequent deterioration in water occurred. Using the 40% solids solution, uniform dried coatings of 2 mil thickness were routinely obtained. More dilute solutions, prepared by adding additional amounts of toluene, were also tested; however, subsequently coated rods allowed too much moisture permeation and slippage of the coating along the glass surface was observed.

The examination of the solvent release characteristics which were needed to determine a diffusion coefficient for the solvent in the Elvacite 6014 coatings, did not prove fruitful. At room temperature and under mild vacuum the coatings have a marked tendency to form pockets of trapped, volatilized solvent which result in bubbles in the coating. This effect is probably the consequence of the surface of the coating drying too quickly and trapping beneath it solvent that is trying to escape from the interior of the coating material. In order for the solvent to be released, it must diffuse through the already solidified outer coating

layer, and this phenomenon results in erroneous weight loss data. Without applying the mild vacuum the coating appears to dry quite uniformly; however, the vacuum is necessary for the measurement of a true weight loss. Because the sample is suspended in a tube of small volume (it cannot be suspended in air due to the sensitivity of the Cahn electrobalance to air currents), it is thought that only small amounts of volatilized solvent will change the atmosphere within the tube and that this will significantly change the solvent release rate for the remaining trapped solvent. At higher temperatures, the same effects were seen again, although more bubbling usually occurred due to the outer surface drying quickly at high temperatures.

The Elvacite 6014 top coating is relatively non-absorbent, Our determinations have shown approximately 0.7 percent water absorption during exposure for 72 hours at 25°C for a coating of 2 mil thickness. A solubility of 0.3 - 0.4 percent in 24 hours for methyl-methacrylate has been cited by Billmeyer (9). In hot water, the coating remains transparent, shows no signs of deterioration, and allows very little dissolution of the sodium silicate glass.

C. Characterization of Successful Coating Composite

Using PVHP as a sub-coating and Elvacite 6014 or Saran as top-coatings proved to be successful since preliminary tests revealed that the coatings did not allow slippage to

occur after hot water exposure and very little dissolution of the glass was tolerated. Elvacite was seen to be the better of the two outer coating formulations due to its better resistance to hot water. Thus, rods, coated with a one mil thickness PVHP under coating and a 2 mil thickness outer coating of Elvacite 6014, were used for several consecutive testing procedures.

In extensive tests using the Elvacite 6014 top coating, after exposure up to two hours, the detected sodium concentration within the test solutions never exceeded one ppm, and all concentrations in excess of 0.5 ppm were attributed to runs at the higher temperatures (65 or 70^{o}C). For purposes of comparison, it may be mentioned that uncoated sodium silicate rods will accumulate one ppm sodium in about 11 minutes (See Figure 9), at 25^{o}C under standard testing procedures including continuous agitation. All these data compare to a typical sodium concentration of 8 ppm in tap water available in this laboratory.

Representative plots of sodium concentration versus immersion time for exposure to distilled water, acidic and basic test solutions are given in Figures 10 through 13. At each solution temperature, the permeation rate was characterized by the slopes of these plots. Due to the changing volume of water caused by the removal of small (10 ml) samples, the graphs should have exhibited an increasing slope; but this effect was found to be virtually

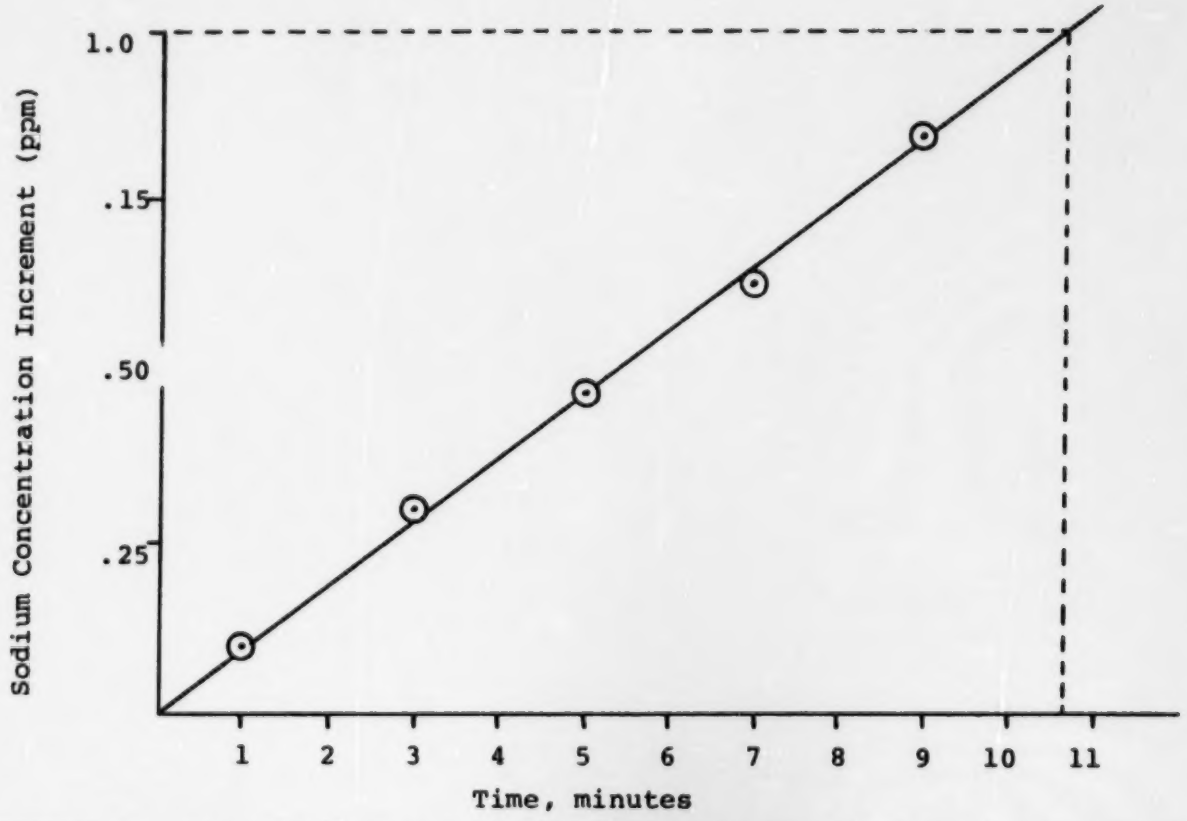


FIGURE 9. Dissolution Rate of 65% SiO_2, 35% Na_2O Glass Rod (approximately 3 mm diameter, at 1 inch immersion) in Water at 25°C with Continuous Agitation.

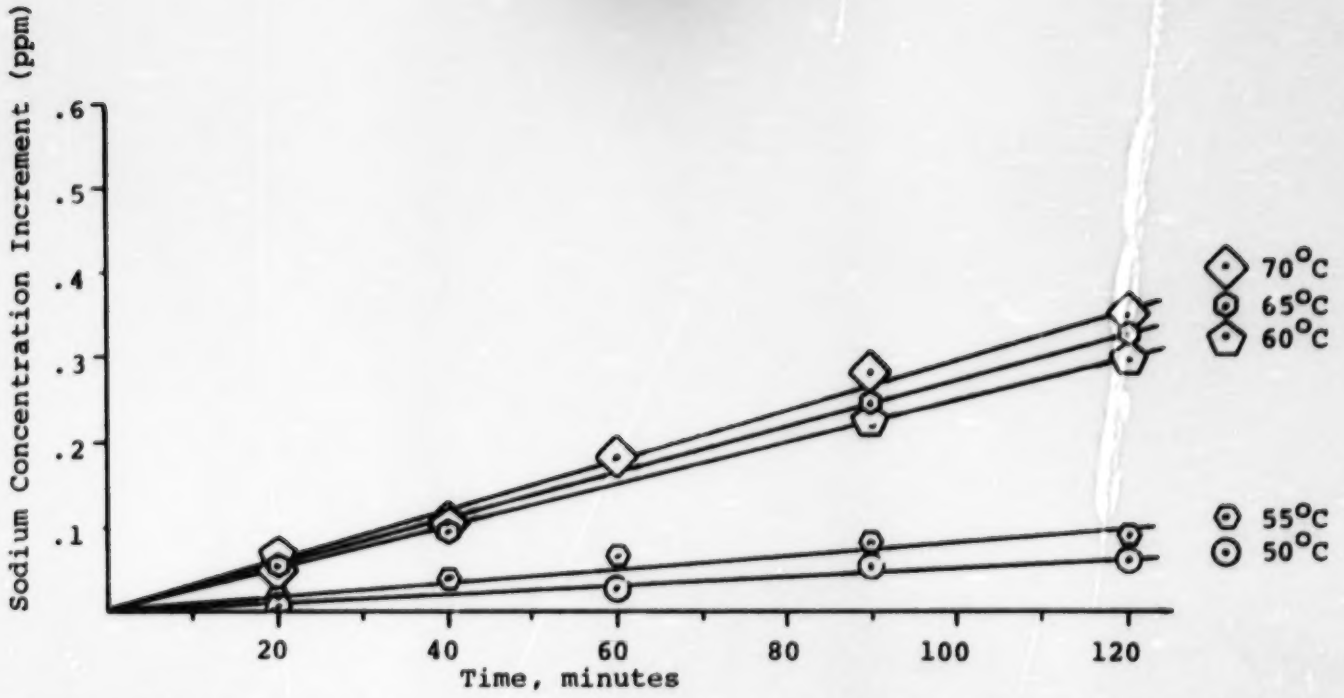


FIGURE 10. Sodium Permeation Rate for PVHP-Elvacite 6014 Coated Rod (approximately 3 mm diameter, 1 inch immersion) in Distilled Water with Continuous Agitation at Various Temperatures.

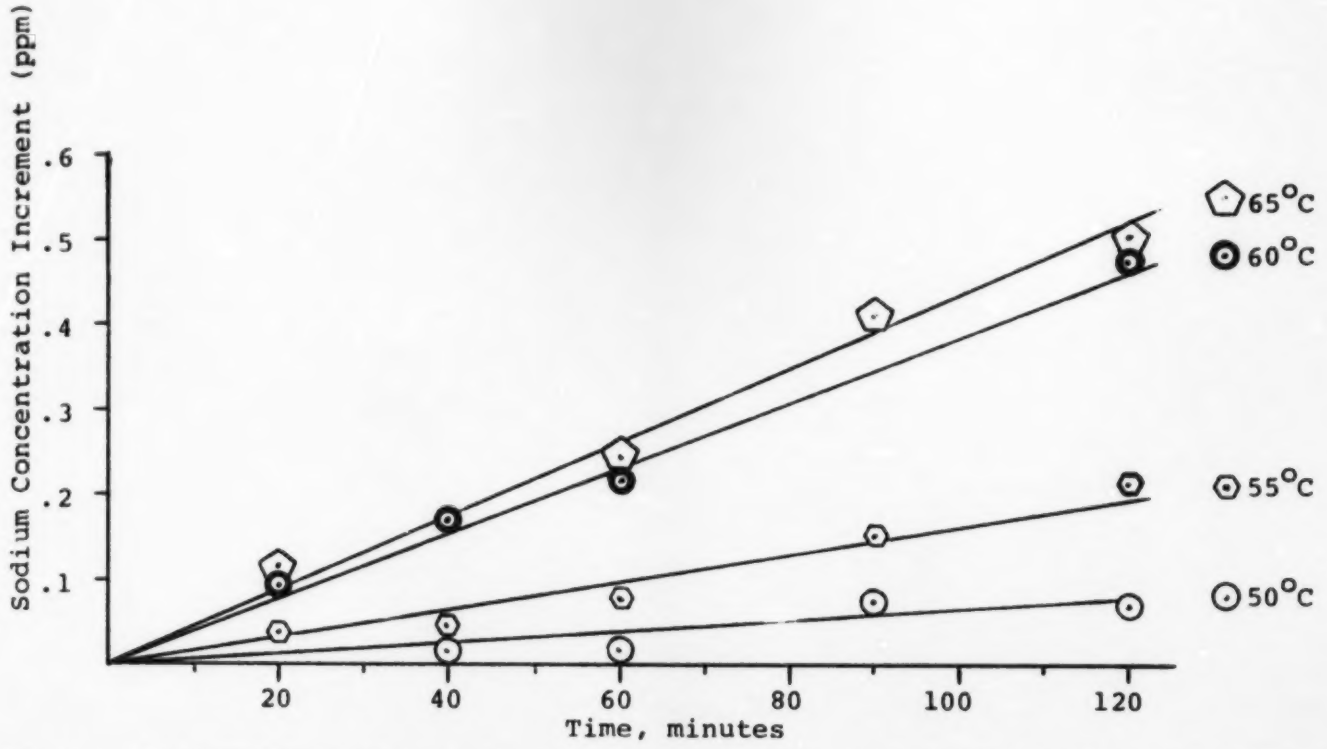


FIGURE 11. Sodium Permeation Rate for PVHP-Elvacite 6014 Coated Rod (approximately 3 mm diameter, 1 inch immersion) in Phosphoric Acid Solution (pH=2.57) with Continuous Agitation at Various Temperatures.

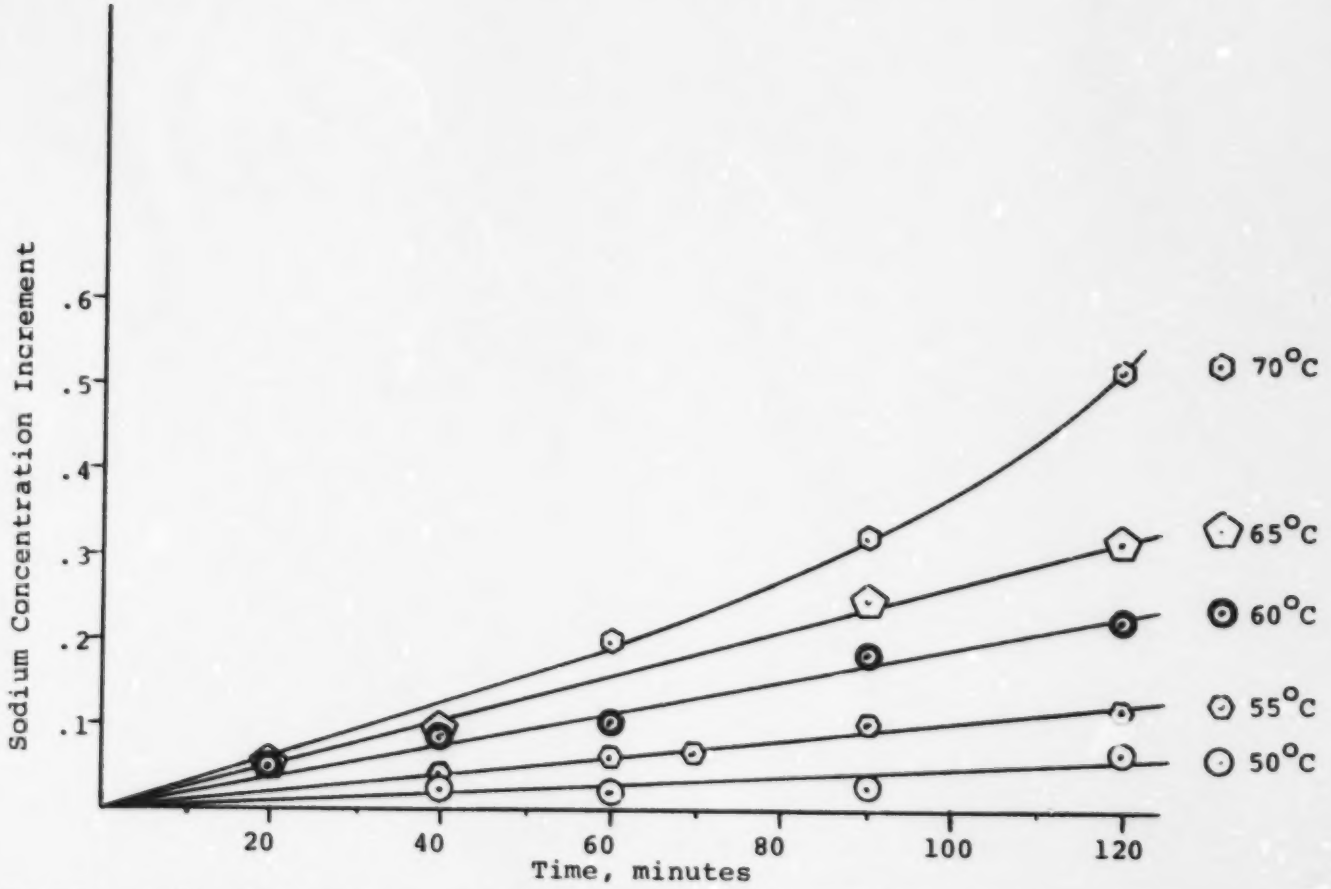


FIGURE 12. Sodium Permeation Rate for PVHP-Elvacite 6014 Coated Rod (approximately 3 mm diameter, 1 inch immersion) in Barium Hydroxide Solution (pH=10.7) with Continuous Agitation at Various Temperatures.

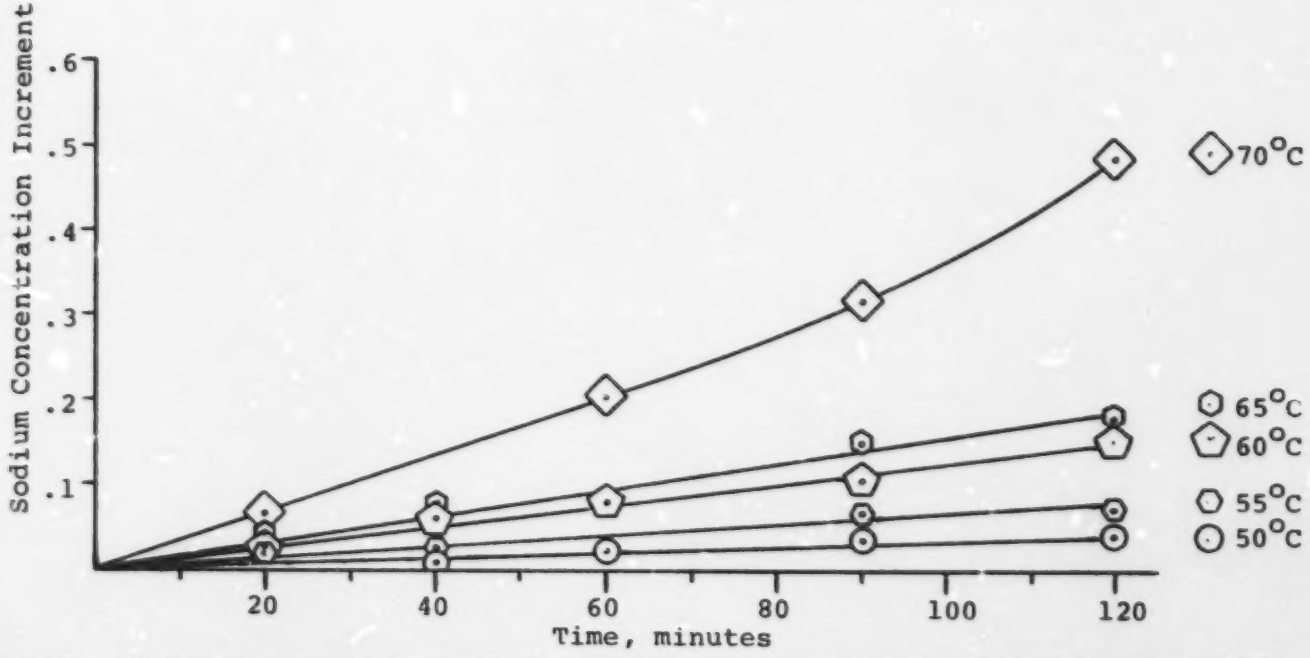


FIGURE 13. Sodium Permeation Rate for PVHP-Saran F-310 Coated Rod (approximately 3 mm diameter, 1 inch immersion) in Distilled Water with Continuous Agitation at Various Temperatures.

undetectable. From the rate data, typical Arrhenius plots were constructed for each series of experiments (see Figure 14). Each graph exhibited a change in slope at 60°C, which is interpreted to be the glass transition temperature for the barrier coating. This temperature is known rather precisely and any uncertainty is limited to ±1°C. At the temperature under discussion, the coating undergoes transition from the glassy state to the rubbery state, and a concomitant change in the temperature dependence of sodium permeation rate is observed. In the rubbery state, the sodium permeation rate is less strongly affected by changes in temperature, due to a smaller activation energy required for permeation. Any significant change of water solubility within the rubbery coating could account for the observed behavior also, since permeability depends both upon the diffusion coefficient and upon solubility within the material matrix (9).

The coating in the glassy state appears to be unaffected by the mild pH changes of the test solutions, since all three series of experiments yielded about the same temperature dependence for the rate of sodium permeation. These findings can be interpreted to mean that the same activation energy applies in all cases in the glassy state. In the rubbery state, the permeation rates were shown to be unaffected by acid and distilled water, but in basic solution the coating apparently weakened at the higher temperatures.

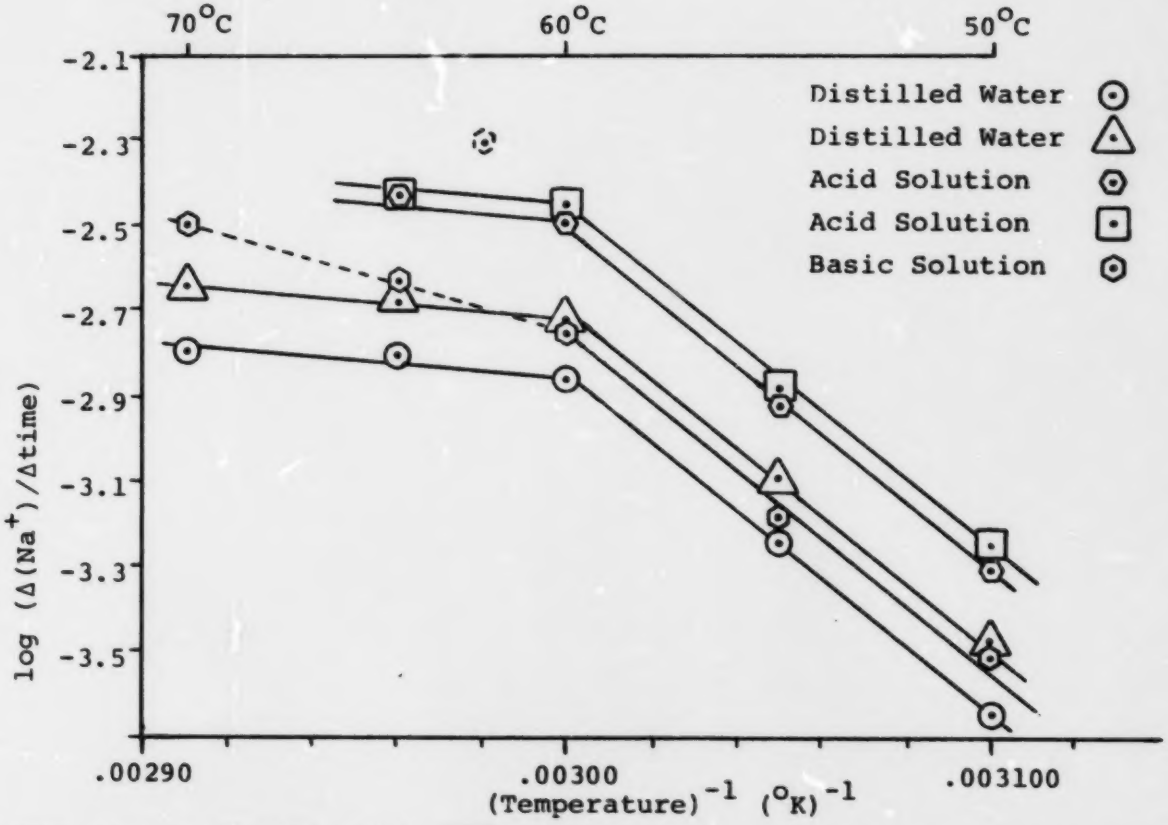


FIGURE 14. Arrhenius Plot to Examine Sodium Permeation Rate as a Function of Temperature and Solution pH.

This effect allowed a greater rate of increase in permeation rate with temperature than had been encountered in other series of experiments. However, the base-initiated phenomena were shown to be history dependent, since re-examination with the same coated rod at a lower temperature (62°C) later exhibited a faster rate than had previously been observed at 70°C (see Figure 14). These observations show that the coating had undergone permanent damage upon exposure to hot basic test solutions. Such degradation phenomena may be due to the formation of cracks and fissures or to a more uniform decrease in the coating thickness during contact by hot basic solutions. Seymour and Steiner (5) point out that acrylic polymers have the tendency to undergo saponification in basic solutions; but it is also reported that methyl-methacrylate is quite resistant to this reaction.

In most of the practical considerations of coating permeability, the glassy state of the polymer is important, since this state usually prevails at the use temperatures for containers, i.e., at room temperature and below. Using the low temperature portion of the Arrhenius plot, an extrapolation can readily be performed to determine the sodium permeation rate at 25°C (see Figure 15). From the extrapolation one calculates a permeation rate of 1.7 ppm sodium per year in volumes of test solution as routinely employed and assuming continuous agitation at all times.

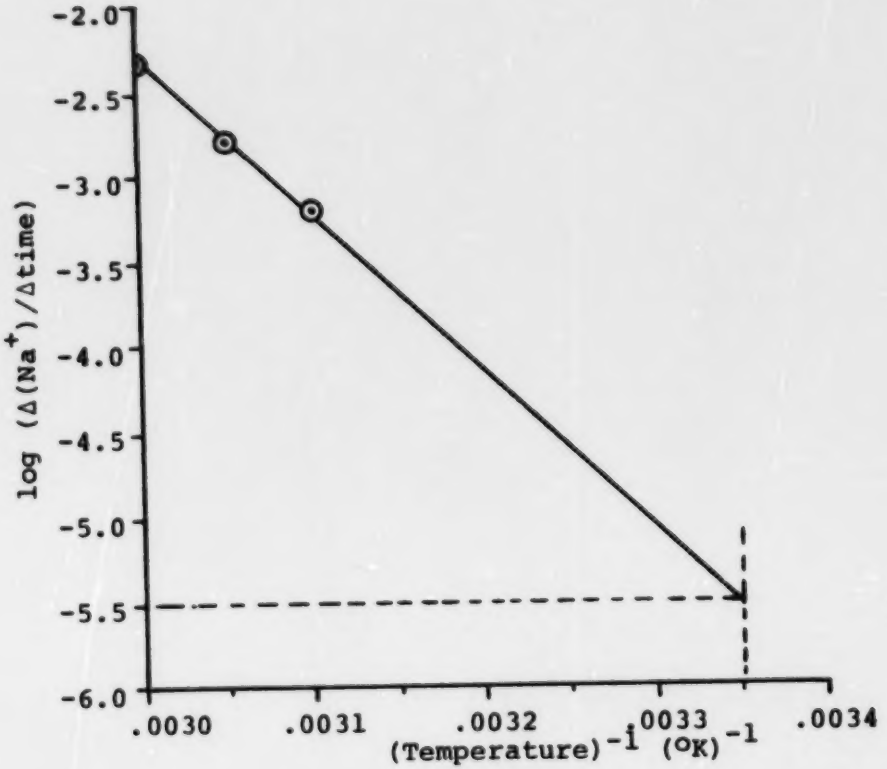


FIGURE 15. Sodium Permeation Rate at Room Temperature in Distilled Water with Continuous Agitation.

Without such agitation the rate is expected to be considerably smaller (3). Using this calculation, any two hour test at 50°C is seen to correspond to exposure at room temperature for approximately fifteen days. Similarly it was found that the 55°C test for two hours corresponds to approximately 45 days, while the 60°C test corresponds to about 105 days at room temperature. Above 60°C the coating is in the rubbery state and data cannot be correlated directly with room temperature data.

The dissolution of 1.7 ppm per year can be contrasted with a calculated dissolution rate of approximately 48,600 ppm sodium per year for an uncoated sodium silicate glass rod (of our standard composition) at 25°C, assuming continuous agitation. In all these calculations it is assumed that the surface area of the rod samples remains constant, although the diameter of the uncoated rods will actually become smaller as dissolution progresses. Idealized calculations of the described nature can also be used to show that an uncoated rod of 0.36 grams will completely dissolve in about 2.9 days at 25°C under continuous agitation.

Evaluation of the slope of the Arrhenius plot permits calculation of the activation energy E_a, since $E_a = -(\text{slope}) \times 2.3\ R$. For the glassy state the activation energy was calculated to be approximately 35 kcals/mol, but for the rubbery state the activation energy was calculated to be significantly lower, i.e., approximately 4 kcal/mol.

Because of deterioration of coatings in alkaline media, the latter type of calculations could only be performed with data from the experimental series that used distilled water and acidic test solutions.

Lubricity of the PVHP-Elvacite coating was evaluated at the Anchor Hocking research facilities. Lubricity of the coating is quite important in the industrial handling of containers, since a low coefficient of friction (good lubricity) at the outer container surface is essential for conducting bottle filling rapidly. The coating lubricity under dry condtions was in the same region as that for dry clean glass surfaces (2), while increased lubricity under wet conditions was observed. The coefficient of friction for the dry coating as measured at the Anchor Hocking facilities was found to be 0.775, while the wet coating exhibited a value of 0.634 whereas a value in the range of 0.80 to 1.00 for glass is cited by Holland (2).

Aside from the fact that the composite coating meets the requirements as a good barrier and has an acceptable glossy appearance, it may be worth noting that the preferred polymer coating formulation (of PVHP and Elvacite 6014) does not contain any chlorine or nitrogen. Instead, it is merely composed of carbon, hydrogen and oxygen. Chlorine, when incinerated, could produce corrosive hydrochloric acid, or poisonous vapors such as phosgene, carbon tetrachloride or chloroform. Nitrogen compounds are equally

objectionable, since cyanogen and other toxic or even carcinogenic materials can be derived from them (30).

One method of accomplishing shatter-proofing for glass has been the use of thin, tightly adhering polymeric coatings: Delmonte (15) states that polyvinyl acetate has been used for this purpose. Therefore, it is seen that the application of our polymeric coating might also provide some shatter-proofing for glass containers.

CHAPTER IV

CONCLUSIONS

1. Etching treatments of the glass surface, thought to involve the laying down of insoluble sulfides or hydroxides on the glass surface through the use of tin, silver, zinc and copper ions, have been used to provide priming treatments for seating of polymeric barrier coatings such as Saran F-310 or Elvacite 6014. Such coatings on rods of soluble glass were shown to allow little dissolution of the glass; furthermore, slippage of the coating along the glass surface was not observed after hot water testing procedures at temperatures up to 70°C.
2. Although etching techniques have been used with moderate success, they are not advantageous for large scale industrial production of containers; the process is slow, hard to optimize and at times irreproducible. Furthermore, it relies upon some dissolution of the glass, and therefore the process is sensitive to temprature, to variations in glass structure and to composition of etching solutions.
3. Organo-silanes and silicones are ideally suited for large scale rapid spraying techniques; however, among those tested only one exhibited moderate success in resisting deterioration in hot water. Such prime coating formulations

subsequently allow slippage of the coating along the glass surface when tested by a hand test.

4. Glass adhesives that are water soluble to even a small extent are not suitable as surface pre-coatings; even the best water barrier films used allow some water permeation in hot water, thus causing coatings to subsequently fail by slippage effects or by ballooning, which result from osmotic pressure phenomena.

5. As a successful undercoating, polyvinyl hydrogen phthalate provides polar carboxyl groups for dipole-dipole interaction with the glass, while its bulky hydrocarbon chain and benzene ring structures virtually prevent dissolution in hot water. PVHP appears suitable for industrial applications as it can be either dip-coated or sprayed onto glass surfaces when in MEK solution. It forms a hard transparent film that provides a good surface for seating barrier coatings.

6. As outer barrier coatings both Elvacite 6014 and Saran F-310 were found to be suitable. Both can be used in solution form for either dip-coat or spray application onto glass surfaces. Elvacite 6014, with its better resistance to hot water, is the more desirable of the two formulations for coating those containers that will be used for beverages, food, etc. Both coating formulations appear to be suited for rapid spraying techniques currently used in industry.

7. The PVHP-Elvacite 6014 composite coating virtually prevents the dissolution of soluble glass rods. At the common use temperatures, i.e., at room temperature and below, it was shown that coated soluble glass containers might have a shelf life comparable to that of commonly used food containers, such as metal cans.

8. An observed change of trends for sodium permeation rates (at approximately 60°C) is thought to occur because the polymeric coating undergoes a change from the glassy to the rubbery state. In doing this, the heat of permeation activation is seen to be lowered; but the observed effect could also be attributed to changes in water solubility within the polymeric matrix and changes in the diffusion constant for water through this matrix.

9. The Elvacite 6014-PVHP coating is merely composed of carbon, oxygen and hydrogen. It should not, therefore, contribute to severe problems during incineration as do many of the common chlorine-containing polymers.

10. Good lubricity of a container outer surface is necessary for the rapid filling of containers. The PVHP-Elvacite 6014 coating has a lubricity in the same range as that of presently used clean dry glass. Furthermore, under wet conditions which might be present during filling operations, the coating exhibits increased lubricity.

11. The total cost of raw materials and processing for both the commonly used soda-lime glass and sodium silicate glass should be approximately equivalent; therefore, the economic feasibility of the water soluble container is directly related to the additional cost accrued due to the polymeric coating and its application. However, this increased cost is also incurred on polymer coated containers presently being developed to provide shatter-proofing. Since the water soluble glass coating might provide shatter-proofing, water soluble glass containers should be able to compete in terms of cost, with future shatter-proof containers. At the present time, there is justification for the use of water soluble glass containers if the cost of litter pick-up and disposal is considered.

CHAPTER V

RECOMMENDATIONS

Future studies of the dissolution products of water soluble glass and their effects upon the environment are currently planned. These studies are necessary before the water soluble bottle can be instituted; in eliminating one environmental pollution problem we must be sure not to create new ones.

Investigations should also be aimed to study the degradation of the coated glass structure. Furthermore, determinations should be conducted to show how pinholes or imperfections in the coating will propagate the dissolution of the glass at the interface with the coating material. It is presently thought that if a continuous coating is ruptured, glass dissolution will at first occur at the exposed glass surface, but will eventually spread along the surface under the coating. It will be interesting to see if the osmotic pressure effect can pry the coating away from the surface at intentionally applied coating imperfections.

Rapid coating techniques and other industrial handling problems should also be examined. The coating lubricity has already been examined, but other prerequisites for the coating, such as scratch resistance, have yet to be evaluated.

The largest problem seen, in terms of the economic feasibility of a water soluble glass container, is that of the increased cost due to the polymeric coating. Future studies should be directed towards a one step coating application. Through the use of mixed solvents, it is thought that the undercoating and outer coating polymer formulations can be combined, so that a one step coating process will be possible. Moser (6) has cited several instances in which a more polar material was combined with a material that exhibited more desirable characteristics (higher strength, non-brittleness, etc.) to yield a better glass adhesive.

Investigations into government regulations on coatings, i.e., F.D.A. approval for the coating to be used on a food container, have also to be conducted; Saran is currently used for food wrappings and Elvacite is thought to be acceptable, but both must be approved for this specific use, in order to dispel any fears of toxicity.

The water soluble glass container with polymeric coatings, should be considered as a reasonable approach to alleviate problems of glass litter; hopefully, future utilization will be effective in the abatement of unpleasant and hazardous glass litter, and this may contribute significantly to improve the appearance of our parks, public grounds and our general environment.

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APPENDIX I

The following chart is a summary of coating treatments that were conducted in order to determine a suitable coating for water soluble glass rods. The coating was required to:

1. coat the glass surface uniformly and continuously,
2. resist deterioration during testing,
3. prevent glass dissolution, and
4. remain adherent to the glass surface.

In the etching pre-treatments, all treated rods were washed in distilled water and air dried before outer barrier coatings were applied; deviations from this standard procedure will be noted in the chart.

All outer coatings were applied as described in the procedure of this paper.

The standard preliminary test procedure was to immerse one inch of the coated rod in 100 ml of 60^{o}C distilled water for 2 hour without agitation; this procedure will be noted as standard condition 1 (S.C. 1). Standard condition 2 used 200 ml of distilled water and continuous agitation; this test procedure usually involved the removal of samples for sodium permeation rate studies. Deviations from these standard procedures will be noted in the chart under time and temperature.

In the results section of the chart, sodium concentration readings, if taken, correspond to samples taken at the end of the test period.

UNDERCOATING OR SURFACE PRETREATMENT	OUTER COATING	TEST CONDITIONS S. C.	TIME	TEMP.	RESULTS
Conc. $CuSO_4$ Na_2S wash	Saran	1	2 hr	60°C	Bubbles in coating, still intact (Na^+) <1.0 ppm
Conc. $CuSO_4$ Na_2S wash	Methyl-2-cyano-acrylate	1	2 hr	60°C	Coating brittle, peeled away from glass
Same as above	Saran-Formvar mixture	1	67	60°C	Coating becomes brown, shiny still intact with bubbling (Na^+) <2.0 ppm
Same as above	Saran (dried under vacuum for better solvent release)		-		Coating bubbled due to rapid drying of the surface.
.5N $AgNO_3$ Na_2S wash	Saran	1	2 hr	60°C	Coating brown after testing - still intact (Na^+) <0.5 ppm
.5N $AgNO_3$	Saran	1	2 hr	60°C	Coating brown after testing, slight bubbling (Na^+) <0.5 ppm
.5N $AgNO_3$ NaCl wash	Saran	1	67	60°C	Coating turns brown, slips from the glass surface (Na^+) >4.0 ppm
.56N $ZnSO_4$ Na_2S wash	Saran	1	2 hr	60°C	Coating remains clear, intact (Na^+) <0.5 ppm

UNDERCOATING OR SURFACE PRETREATMENT	OUTER COATING	TEST CONDITIONS S. C.	TIME	TEMP.	RESULTS
.56N $ZnSO_4$ KOH wash	Saran	1	2 hr	60°C	Coating remains clear, intact (Na^+) <0.5 ppm
.56N $ZnSO_4$	Saran	1	2 hr	60°C	Large blush, coating is split (Na^+) >4.0 ppm
Conc. $CuSO_4$ Na_2S wash	Saran (acetone solvent)		-		Although the acetone was used for better solvent release, bubbling of the coating occurred using normal drying procedures.
.56N $ZnSO_4$ KOH wash heat rod to 50°C	Saran		-		Bubbling occurred in the coating on drying.
.56N $ZnSO_4$ KOH wash	GE "Dri Film" 88	1	2 hr	60°C	Coating peeled away from glass surface
.56N $ZnSO_4$ KOH wash	Formvar	1	2 hr	60°C	Coating became brittle, chipped
Same as above	Du Pont Elvacite 6014	1	2 hr	60°C	Coating remains clear and intact (Na^+) <0.5 ppm
Same as above	Catalin 1005	1	2 hr	60°C	Coating became brittle, peeled away from glass
Same as above	Catalin A-1136	1	2 hr	60°C	Coating blushes, bubbles form

UNDERCOATING OR SURFACE PRETREATMENT	OUTER COATING	TEST CONDITIONS S. C.	TIME	TEMP.	RESULTS
Same as above	GE SC-77 (vapor deposited)	1	2 hr	60°C	Coating becomes whitish, peels away from glass
Same as above	GE SC-77 (vapor deposited)	1	2 hr	60°C	Same as above
Same as above	GE SC-77 (applied in solution with petroleum ether)	1	2 hr	60°C	Same as above
.56N $ZnSO_4$ KOH wash	GE SC-87 (applied in solution with petroleum ether)	1	2 hr	60°C	Coating becomes whitish, peels away from surface
Same as above	Eschem-methyl methacrylate SR-100, Type 12	1	2 hr	60°C	Coating becomes brittle, chipped
Same as above	Eschem-ethyl methacrylate	1	2 hr	60°C	Coating becomes brittle, white, peels away from glass surface
Conc. $ZnCl_2$ Na_2S wash	Elvacite 6014	2	3 hr	50°C 60°C	Coating intact (Na^+) <0.5 ppm
Same as above	Union Carbide A151 vinyltriethoxy-silane	1	3 hr	60°C	Coating dissolved and peeled away from the glass surface

UNDERCOATING OR SURFACE PRETREATMENT	OUTER COATING	TEST CONDITIONS S.C.	TIME	TEMP.	RESULTS
Same as above	Union Carbide A150-vinyltri-chloro-silane	1	3 hr	60°C	Same as above
Same as above	Union Carbide A172-vinyl-tris-(beta-methoxy-ethoxy) silane	1	3 hr	60°C	Same as above
Conc. $MgSO_4$ etch KOH wash	Elvacite 6014	1	22 hr	60°C	Slight bubbling and deterioration of the coating near end of rod
Conc. $SnCl_2$ Na_2S wash	Elvacite 6014	1	22 hr	60°C	Coating still intact
Conc. $Ni(C_2H_3O_2)_2$ NaS wash	Elvacite 6014	1	3 hr	60°C	Coating contains bubbles, some peeling of the coating has occurred
Conc. $Ni(C_2H_3O_2)_2$ Na_2S wash	Elvacite 6014	1	2 hr	60°C	(Na^+)>3.0 ppm
Conc. $ZnCl_2$ Na_2S wash	Elvacite 6010	1	2 hr	60°C	Bubbles formed in coating (Na^+) over 4.0 ppm
Same as above	Elvacite 6012	1	2 hr	60°C	Coating blushes, cracks
Same as above	Elvacite 6016	1	3 hr	60°C	Coating has peeled away from the glass surface (Na^+) >4.0 ppm

UNDERCOATING OR SURFACE PRETREATMENT	OUTER COATING	TEST CONDITIONS S.C.	TIME	TEMP.	RESULTS
GE SC-77 (vapor deposited)	GE SC-87 in petroleum ether solution	1	2 hr	60°C	Coating has dissolved and peeled away from the glass surface
Same as above	Union Carbide A151 Silane	1	2 hr	60°C	Same as above
Union Carbide A150	Elvacite 6014	1	2 hr	70°C	Slight amount of bubbling. Coating slips from glass surface with slight pressure, (Na^+) <1.0 ppm
Union Carbide A151	Elvacite 6014	1	2 hr	60°C	Coating intact, but slips from the glass surface with slight pressure, (Na^+) <0.5 ppm
Union Carbide A172	Elvacite 6014	1	2 hr	60°C	Coating intact, but slips from the glass surface with moderate pressure, (Na^+) <0.5 ppm
Union Carbide A172	Elvacite 6010	1	2 hr	60°C	Coating intact, but has swelled away from the glass surface, fails the slippage test.
Union Carbide A172	Elvacite 6012	1	2 hr	60°C	Coating has cracked, slips easily
Same as above	Elvacite 6013	1	2 hr	60°C	Coating has peeled away from the glass surface

UNDERCOATING OR SURFACE PRETREATMENT	OUTER COATING	TEST CONDITIONS S.C.	TIME	TEMP.	RESULTS
Same as above	Elvacite 6016	1	2 hr	60°C	Coating has cracked, and peeled away from the glass surface
GE SC-77 (vapor deposited)	Elvacite 601	1	3 hr	65°C	Coating failed by slippage
Valchem Chrome Stearate	Elvacite 6014	1	2 hr	60°C	Coating intact, but can be slipped from the glass rod
Union Carbide A172	Saran	1	2 hr	60 C	Coating intact, but fails slippage test
Valchem Chrome Stearate	Saran	1	2 hr	60°C	Saran can be slipped away from the chrome stearate (Na^+) <1.5 ppm
Union Carbide A151	Saran	1	2 hr	60°C	Coating intact, but fails slippage test
Elvanol (71-30) DuPont polyvinyl alcohol	Saran	1	2 hr	60°C	Coating intact, but fails slippage test
Same as above	Elvacite 6014	1	2 hr	60°C	Coating intact, but fails slippage test
Elvanol (52-22)	Elvacite 6014	2	2 hr	60°C	Coating intact, but fails slippage test
Benzoic acid etch	Elvacite 6014	1	2 hr	60 C	Coating slips, (Na^+) >4.0 ppm

UNDERCOATING OR SURFACE PRETREATMENT	OUTER COATING	TEST CONDITIONS S.C.	TIME	TEMP.	RESULTS
Hydrochloric acid etch	Elvacite 6014	1	2 hr	60°C	Coating slips
Bakelite XYHL polyvinyl butyral with dibutyl phthalate added	Elvacite 6014	2	2 hr	60°C	(Na^+) 1.5 ppm, but coating slips
Same as above	Saran	2	2 hr	60°C	(Na^+) 1.5 ppm, but coating slips
Bakelite XYHL mixed with Saran in MEK	-	2	2 hr	60°C	Coating slips
Same as above	Elvacite 6014	2	2 hr	60°C	Same as above
Polyvinyl hydrogen phthalate (Eastman organics) dissolved in MEK	Elvacite 6014	2	2 hr	60°C	Coating intact, does not slip away from glass surface
Same as above	Saran	2	2 hr	60°C	Same as above

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ABSTRACT

A suitable polymeric coating to render sodium silicate, water soluble glass usable as a container material for such products as soft drinks, food, etc., has been experimentally determined. The coating consists of two polymeric materials: 1) an undercoating, polyvinyl hydrogen phthalate applied in methyl ethyl ketone solution, provides polar carboxyl groups for dipole-dipole interaction with the glass surface while its bulky hydrocarbon chain and benzene ring structures virtually prevent dissolution in water, and 2) an outer barrier coating, Elvacite 6014, a methyl methacrylate copolymer with some butyl methacrylate groupings. Furthermore, additional amounts of carboxyl groups are also present to promote adhesion onto polar surfaces. In addition to Elvacite 6014, Saran F-310, a vinylidene chloride-acrylonitrile copolymer (82.5% vinylidene chloride, 17.5% acrylonitrile as determined by CHN analysis) was also found suitable as a top coating, though it is more hot water sensitive than the Elvacite formulation.

Coated sodium silicate glass rods were tested extensively by immersion in hot aqueous solutions (distilled water, acidic solution, pH=2.57 and basic solution, pH=10.7). Glass dissolution rates, as measured by sodium

ion concentrations in removed samples, were determined versus immersion time. From this rate data, typical Arrhenius plots for the PVHP-Elvacite 6014 coated rods, were constructed for each series of experiments. Each graph exhibited a change in slope at approximately 60°C, which is interpreted to be the glass transition temperature for the barrier coating.

The PVHP-Elvacite 6014 coating composite virtually prevents dissolution of the glass surface. Calculations have shown that a 3 mm diameter coated rod tested at 25°C with continuous agitation allows a sodium permeation rate of approximately 1.7 ppm per year, while an uncoated sodium silicate glass rod (65% SiO_2, 35% Na_2O), is calculated to dissolve at a rate which yields a sodium concentration of approximately 48,600 ppm per year. This compares to a sodium concentration in tap water available in the university system of approximately 8 ppm.

For demonstration purposes, sodium silicate glass tumblers were manufactured by the Anchor Hocking Glass Company (Lancaster, Ohio) and coated with the PVHP-Elvacite 6014 coating. Lubricity tests of the coatings were performed at the Anchor Hocking research facilities and a coefficient of friction comparable to clean, dry glass surfaces was determined; under wet conditions increased lubricity was observed.